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1 JULY - 30 SEPTEMBER 1963

ELECTROCHEMICAL STUDIES IN THE
SYNTHESIS OF N-F COMPOUNDS

Contract No. Nonr-4054(00)
Research Project No. RR001-06-02
ARPA Order No. 399, Program Code No. 2910

November 20, 1963

T R A C O R, I N C.

1701 Guadalupe St.

Austin 1, Texas

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TRACOR, INC.

1701 Guadalupe St Austin 1, Texas

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11 November 20, 1963,

Prepared by:

10 by Robert R. Annand
Robert R. Annand,
Senior Chemist

Approved by:

Ray M. Hurd
Ray M. Hurd
Director of Chemical
Research

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Abstract

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The work reported ~~has~~^{was} been primarily devoted to seeking more reproducible passivation of aluminum electrodes. On the basis of previous work, aluminum was selected as a metal which came close to exhibiting the desired passive behavior in AHF similar to ferrous materials in aqueous systems. Data ~~is~~^{are} reported concerning the reliability of the ~~platinum~~^{Pt} base electrode, and describing the complex behavior of the $\text{Al}/\text{AlF}_3/\text{AHF}/\text{supporting electrolyte}$ system. These data lead to the conclusion that the ~~aluminum~~^{Al} behavior is more like that of the valve metals (e.g., ~~tantalum~~^{Ta}) than that of passivating materials in aqueous systems. It is further concluded that it will be necessary to find either a combination of operating procedure and acidic supporting electrolyte, or a better metal or alloy which will develop a more nearly self-limiting film growth, so that complex, time variable impedance effects are minimized. From analysis of the available data, guidelines for these experiments are discussed based on the mechanism of passive film formation which requires two ionic oxidation states with the anodic product of the higher state less soluble than that of the lower. ←

ELECTROCHEMICAL STUDIES IN THE SYNTHESIS OF N-F COMPOUNDS

I. INTRODUCTION

In the second quarterly status report, it was concluded that of the metals tested, aluminum came the closest to exhibiting a passive behavior similar to ferrous materials in aqueous solutions and was therefore the most likely candidate for a useful electrode for electrode-kinetic studies in AHF. Furthermore, one experiment was reported in which an anodic current wave was observed on constant potential polarization of NH_3 -containing solutions using the aluminum electrode. The current increased after addition of NH_3 gas to the nitrogen stream passing through the cell. However, it was stated that more reproducible passivation of the aluminum electrodes would have to be obtained and the behavior of these electrodes would have to be checked in the presence of the supporting electrolyte (necessary for the kinetic studies) before the characteristics of an NH_3 wave could be fully determined.

The work of the present quarter has been concentrated in these areas, and the results are reported here from those experiments, from a statistical study of the stability of the platinum base electrode, and from the determination of the film resistance as a function of anode potential. These data have produced the conclusion that the Al/AlF_3 electrode system is a very complex one in AHF and more nearly similar to valve electrode systems (e.g., tantalum) in aqueous media than to passive ferrous materials. Our experience to date indicates that many metals (if not most) exhibit this behavior, and that galvanostatic experiments (such as chronopotentiometry) are obviated thereby for the determination of kinetic parameters of an electroreaction involving soluble species.

II. RELIABILITY OF THE PLATINUM BASE ELECTRODE

In constructing the electrode assemblies for the electrolytic cell, dual platinum electrodes have been included in several models so that the potential difference between them could be used as a measure of the stability of the platinum base electrode system. Potential measurements were made with a Keithly high-impedance electrometer (10^{14} ohms) at the same times that the potentials of the aluminum electrodes were recorded. The sign of the potentials was taken with respect to the same platinum electrode used for the base in the aluminum potential measurements. The results for fourteen different experiments on fourteen days are recorded in Table I. It may be seen from these that the average potential difference for the fourteen different days range from -445 mv to +370 mv. Further examination of the results shows no readily apparent trends related to the presence of H_2O , NH_3 , $NaHF_2$, or combinations of these. However, the fact that the average difference is only +28 mv, taking the measurements as a whole group, leads to the suspicion that there are factors which influence the measurements which have not been taken into account.

Accordingly, the data were treated further statistically to reveal the likelihood of such factors. These results are presented in Table II. The standard deviation of the whole group reflects numerically the wide range of the variations of the measurements. By statistically pooling the results, the standard deviation of the pooled group reflects the average precision of the measurements taken all on one day. This number indicates that measurements taken all on one day are more likely to be consistent than those taken across several days. Application of the F Ratio test confirmed this indication (ref 1).

In order to locate the variations, the data for the three sets of fresh electrodes were treated separately and tested by F Ratio. These results (also given in Table II) show that the measurements on the three separate days are not significantly less precise than those of the group taken as a whole.

TABLE I
POTENTIAL DIFFERENCE BETWEEN Pt WIRES IMMersed IN AHF

Run No.	Avg. Pot. Diff. (mv w.r.t. Base)	Standard Deviation (mv)	No. Measmts	Time Span of Measmts (hrs)	Remarks
1	-9.0	57	53	3-1/2	Fresh electrodes-Potentiostatic Al curve.
2	+89	58	47	8	Same electrodes-Potentiostatic Al curve.
3	-75	132	38	7	Same electrodes-Potentiostatic Al curve.
4	-3.7	44	87	7	Fresh electrodes-Galvanostatic Al curve.
5	-1.1	11	68	8-1/4	Same electrodes-Galvanostatic Al curve.
6	-206	152	60	7-1/4	Same electrodes-Galvanostatic Al curve.
7	-445	144	41	6-1/2	Same electrodes-Fresh AHF-Potentiostatic Al curve.
8	+87	42	36	6-3/4	Same electrodes-Same AHF-Potentiostatic Al curve.
9	-9.4	62	70	9	Same electrodes-Same AHF-NH ₃ added-Potentiostatic Al curve.
10	-31	6.7	36	5-1/4	Same electrodes-Fresh AHF-NH ₃ and NaHF ₂ added-Potentiostatic Al curve.
11	+20	1.8	26	4	Fresh electrodes Fresh AHF plus NaHF ₂ -Potentiostatic Al curve.
12	+284	110	53	7-1/2	Same electrodes-Same AHF plus NaF ₂ -H ₂ O added-Potentiostatic Al curve.
13	+306	112	58	7-1/2	Same electrodes-Same AHF plus more H ₂ O added-Potentiostatic Al curve.
14	+370	149	31	7-1/4	Same electrodes-Fresh AHF plus NaHF ₂ and NH ₃ -Potentiostatic Al curve.

TABLE II
STATISTICAL DATA CONCERNING THE POTENTIAL MEASUREMENTS

Platinum vs Platinum

Average of all measurements	+ 28 mv
Standard deviation of whole group	155 mv
Standard deviation of pooled group	91 mv

Average of all measurements on fresh electrodes	- 77 mv
Standard deviation of whole group	58 mv
Standard deviation of pooled group	40 mv

Average of all measurements in fresh AHF	+ 10 mv
Standard deviation of whole group	174 mv
Standard deviation of pooled group	67 mv

Aluminum vs Platinum
(at open circuit)

Average of all polarization experiments	-214 mv
Standard deviation	90 mv

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In calculations which ignore the kind of electrodes but consider only experiments with fresh AHF, the standard deviations indicate that the day-to-day differences still exist in this group. It appears that even with the relatively high impedance of our potentiostat, enough polarization of the reference electrode occurs to hasten fluoride film formation and hence alter the reference potential. By using a platinum base electrode which is cleaned daily, the reproducibility should be increased. Modification of the cell design is in progress to provide for this (see section on cell modification, p. 21).

III. BEHAVIOR OF ALUMINUM ELECTRODES

Also included in Table II are the results from averaging all of the open circuit measurements taken on aluminum electrodes at the beginning of the experiments or after standing for a long time following anodic or cathodic polarization. The standard deviation for these measurements is almost identical with that for the pooled group of platinum potential measurements. This result shows that the aluminum potential is at least as stable as the platinum base potential and probably more so.

The picture of the open circuit potential for the aluminum electrodes is complicated by the fact that they do not readily come back to the same value obtained at the beginning of the experiment after polarization either cathodically or anodically. All of the electrodes, fresh or fluoride coated, exhibited a potential within the range indicated in Table II if it was measured either after introduction of fresh AHF to a dry electrode or after having remained in the AHF at least overnight. If however, the open circuit potentials (or the equivalent zero current potentials) were measured immediately following a period at high anodic or cathodic potential, the open circuit potential drifted with time in the manner shown in the examples of Figures 1 and 3. The behavior of the film resistance as a function of time after anodizing is also shown in Figure 3A.

It is unlikely that local high concentrations of dissolved gases are contributing to this potential behavior because a porous Teflon divider has been provided between the aluminum- and platinum-electrode compartment and the nickel screen counter-electrode compartment. Separate nitrogen lines for each have also been provided, and both compartments are constantly swept with nitrogen. The decay times are such that it is also unlikely that physically adhering bubbles of gas fully account for the potential difference, although their desorption may account for the initial rapid drop in the potential. It seems more likely that gas

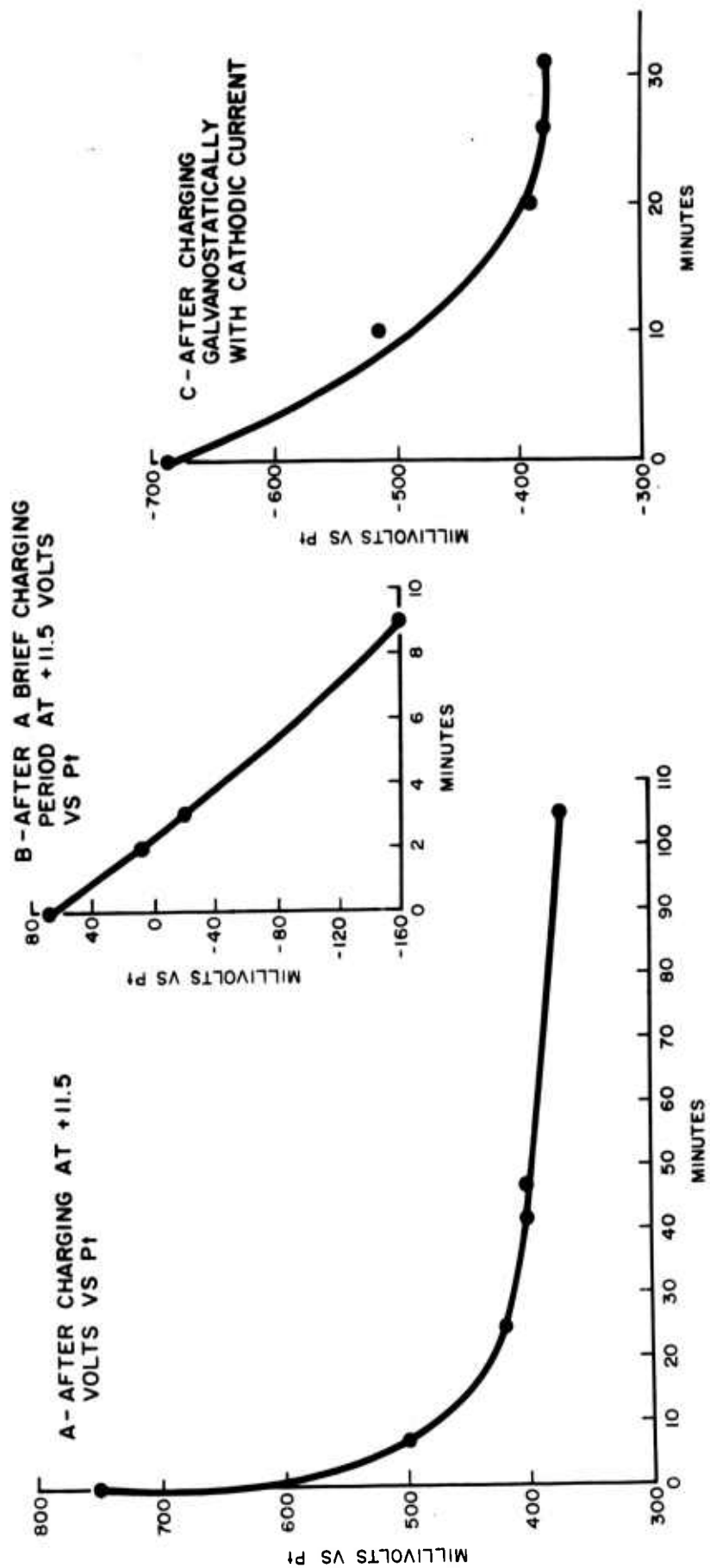


Fig. 1 - VARIATION OF THE OPEN CIRCUIT POTENTIAL OF THE
Al/AlF₃ ELECTRODE

molecules (or atoms) absorbed in the fluoride film contribute to the potential, and that therefore the slow decay time is governed by the rate of diffusion from the bulk to the film-electrolyte interface. This conclusion is supported by the observation that the rate of change of potential with time after the initial drop is not affected by changing the stirring rate by means of the nitrogen flow.

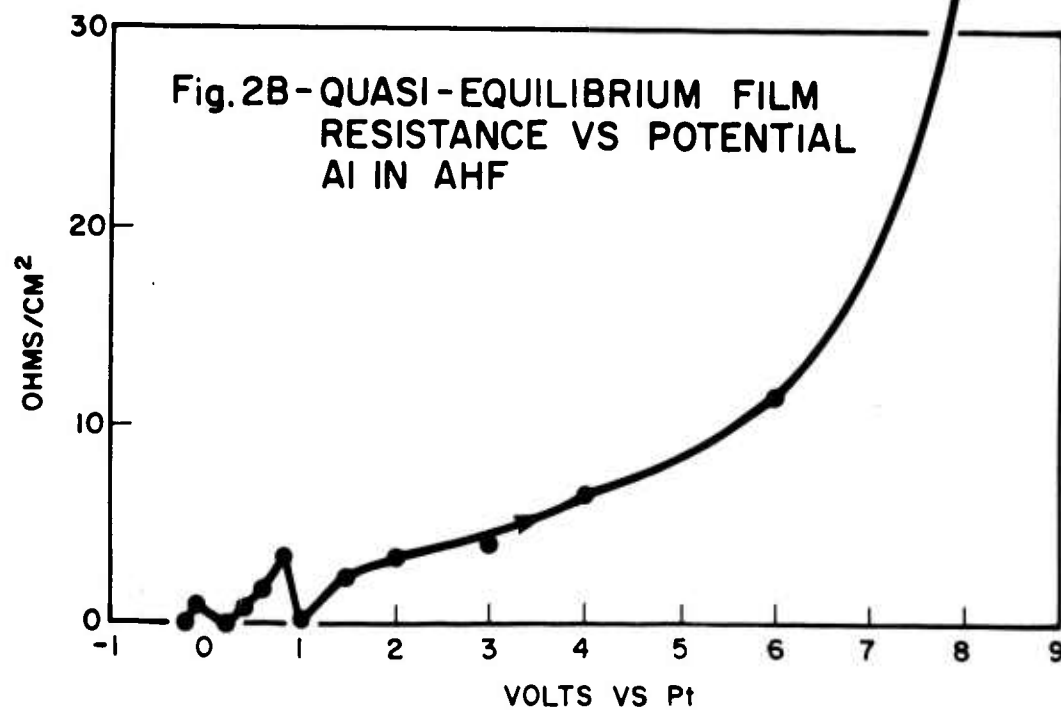
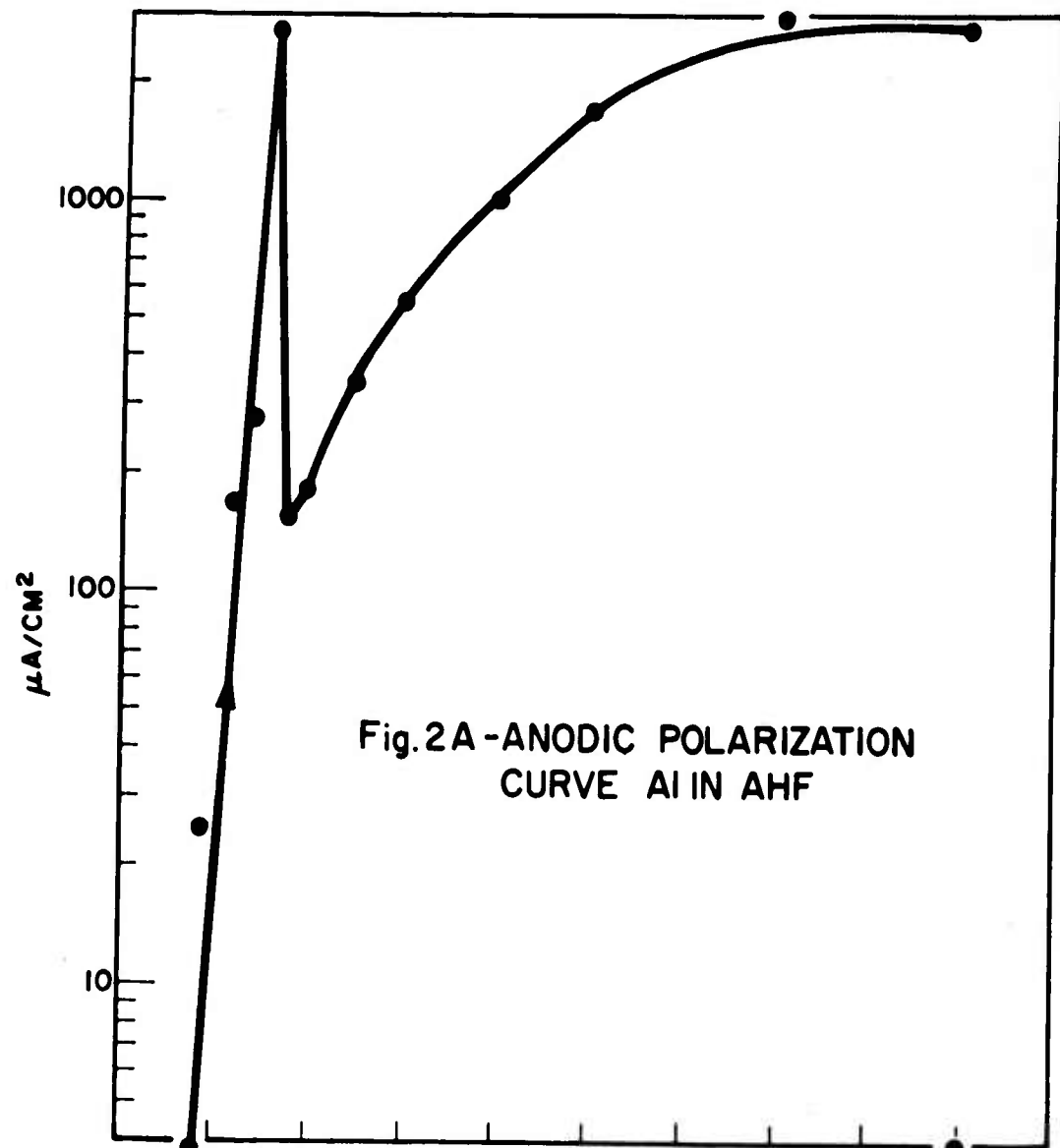
When hydrogen atoms or molecules are assumed to be absorbed after cathodic charging, and thereby are imposing a potential which is dependent on the log of the ratio of film concentrations of H and H^+ , examination of the Nernst potential relationships shows that the potential is expected to shift in the positive direction as the hydrogen concentration decreases by diffusion. Similarly, if absorbed fluorine atoms or molecules are produced on the anodic side of the open circuit potential, the potential would be expected to move in the negative direction as these species diffuse through the AlF_3 layer and are swept away by the sparging nitrogen. The observed shifts in the open circuit potential after charging are in the appropriate directions for such behavior. Similar shifts would be expected for a buildup in hydrogen ion concentration in the film after depletion by cathodic charging or a decrease in free aluminum ion concentration after generation at high anodic potentials. However, by analogy to the valve metal situation in aqueous systems, a high field through the film is expected to be necessary for ionic diffusion, and this is not the case for our measurements which were made at open circuit. These arguments lead to the conclusion that some fluorine is generated on anodic polarization and that it can be intimately associated with the surface AlF_3 film. This would increase the possibility of electrofluorination by interaction of the reactant and the electrogenerated fluorine.

Measurements of the film resistance have been made simultaneously with the taking of an anodic polarization curve. Plots from these measurements of the resistance per unit area and of

log current density are shown vs the same voltage scale in Figure 2. The significant thing about these plots is that, although appreciable resistance is exhibited at low potentials, it does not begin to grow rapidly until the region between +6 and +8 volts is reached. This corresponds to the region where the current levels off in the polarization curve.

It should be born in mind that each of the data points in Figure 2 was obtained after the current had reached an equilibrium value as shown by recorded current-time (i-t) traces. Immediately after the i-t trace had leveled off at +8 volts, the circuit was opened and both the resistance and potential were recorded as a function of time. These data are shown in Figure 3. The constant resistance indicates that the potential decay is not determined by changes in the film resistance such as might be expected for some kind of decay of excitons in a semiconducting film.

Low power, microscopic examination of the three sets of electrodes after they were withdrawn from the cell showed evidence of possibly two types of fluoride layers. The one next to the metal was very fine grained and nodular on the surface. In patches, there was another glassy layer with pock marks which may have been caused by gas bubbles. This was particularly true of the electrode which had been used in the galvanostatic experiments. In no case did the metal-fluoride interface appear to be particularly irregular.



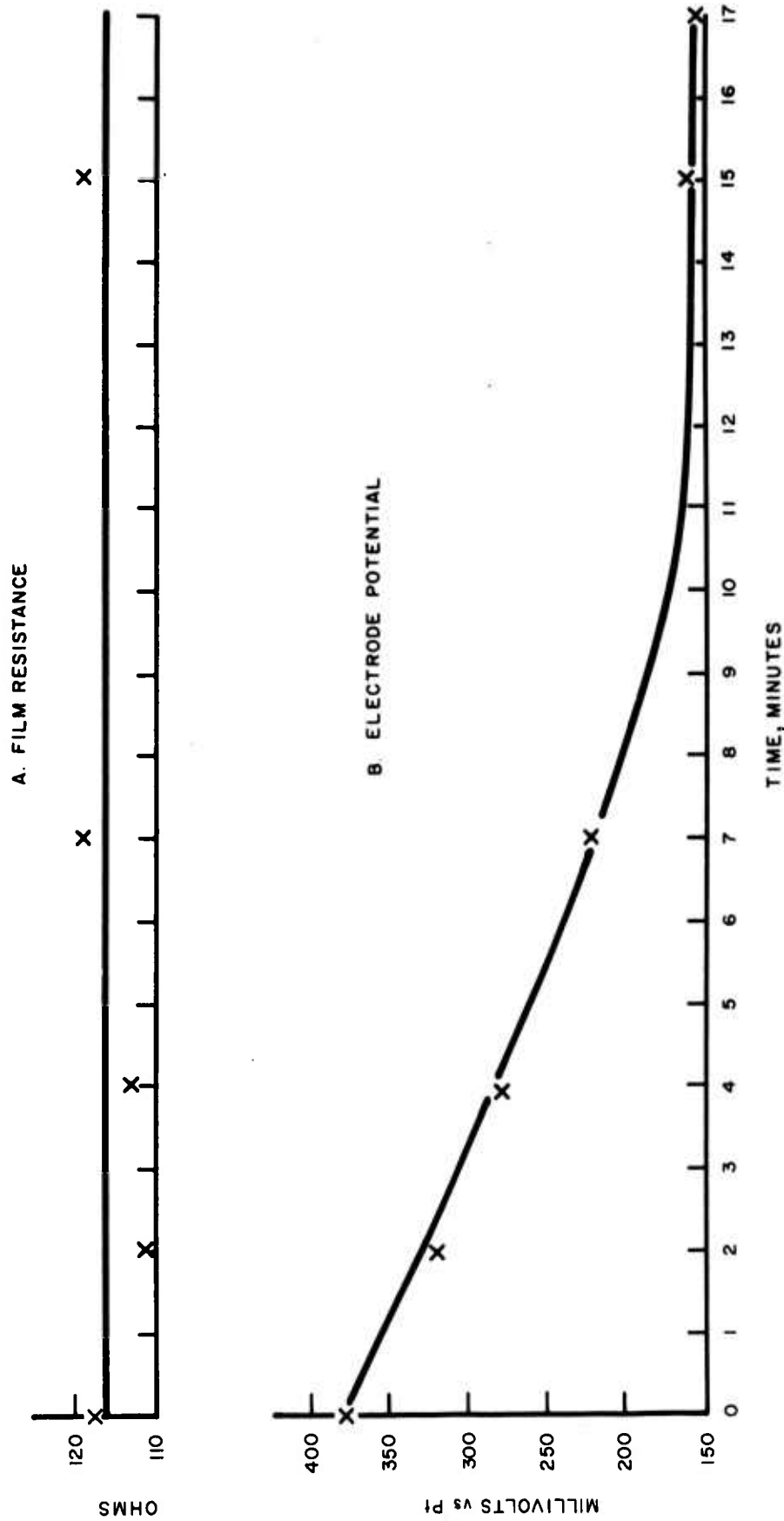


Fig. 3 - MEASUREMENT OF THE OPEN CIRCUIT POTENTIAL AND FILM RESISTANCE OF AN Al/AlF_3 ELECTRODE AFTER CHARGING AT +8.0 VOLTS vs Pt.

IV. POLARIZATION BEHAVIOR OF THE ALUMINUM ELECTRODES

Several polarization curves were made galvanostatically and many, potentiostatically. In the galvanostatic experiments, the cathodic branch of the curve was very similar to those of the potentiostatic curves, but the anodic behavior was quite different. In the galvanostatic case, even at very low current, the potential of the electrode moved in the positive direction with time, rapidly at first and then progressively more and more slowly. As the current was increased, the total span of voltage covered by the rapid polarization became larger and larger until at 1 ma, the average rate of change of potential was 880 mv/min. At 44 volts, the experiment was terminated. This behavior obviates any attempt to gain kinetic information about the NH_3 reaction by a galvanostatic method, such as chronopotentiometry, using aluminum electrodes. Our experience to date with other metals (e.g., silver, tantalum, tungsten, iron, and nickel) indicates that they either exhibit similar behavior or corrode very rapidly in which case the corrosion current would obscure the reaction current due to the NH_3 electroreaction.

Nevertheless, the possibility still exists for using potentiostatic techniques to obtain the kinetic parameters if operating procedures and conditions can be found which give reproducible electrode behavior in the absence of the NH_3 . Multiple potentiostatic polarization curves were taken with this aim in mind. Using the procedure previously described (p. 9 and ref 2), typical results are presented in Figure 4. In that figure, Curve 1 was taken on a fresh electrode immediately after exposure to the AHF. Curve 2 was taken on a fresh electrode after it has remained in contact with the AHF overnight. Curve 3 is from the same electrode as for Curve 2 and was taken in the reverse direction, i.e., from positive to negative potentials, on the following day. Curve 4 was taken on the third day, again on the same electrode. All of curves were made in solutions containing no supporting electrolyte.

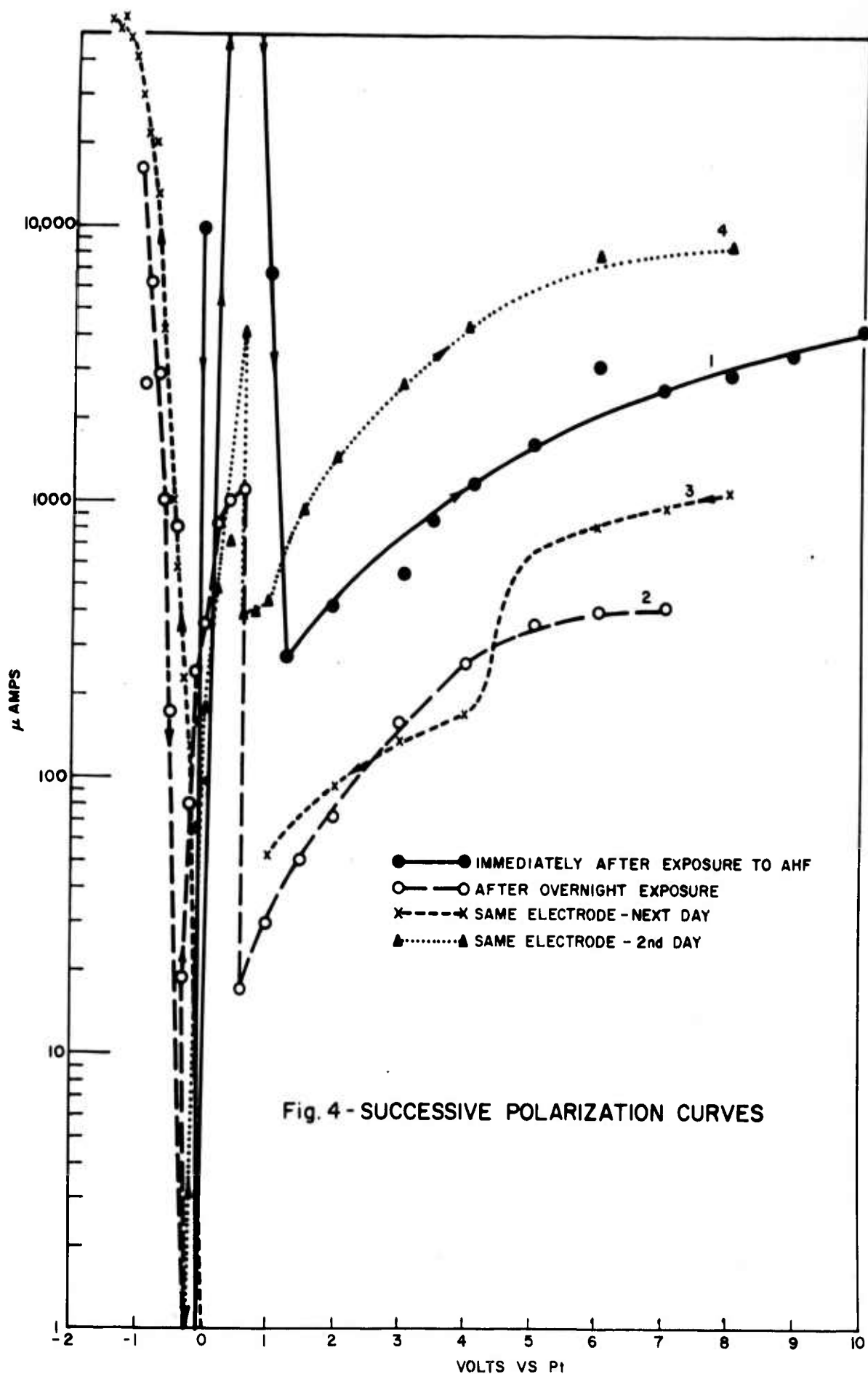
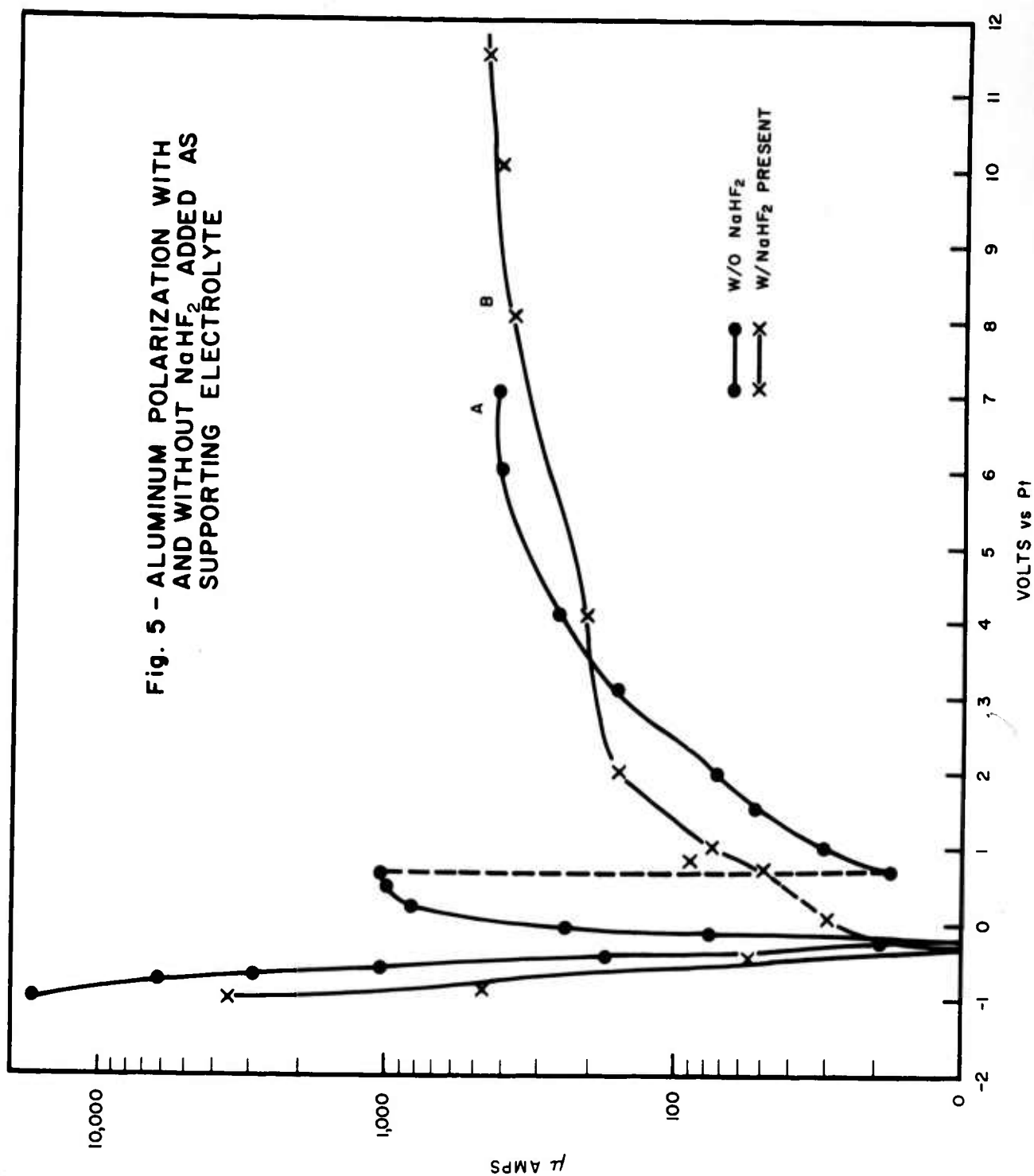


Fig. 4 - SUCCESSIVE POLARIZATION CURVES

Each point on these curves represents the current obtained after the current-time trace had leveled out either to a constant current or to a very slow decrease. This procedure involves as much as an hour's waiting time for each point, particularly at the higher positive potentials, and hence, one curve per day is about maximum output using this procedure. Even so, the reproducibility is not encouraging since the curves are spread by more than an order of magnitude, and the changes do not appear to be progressive.

With electrodes which have been used even more extensively, the anodic current spike becomes uncertain, but the spread between successive curves is narrower in the anodic region from about +1 volt. The open circuit potentials are more variable, however. Typical curves under these conditions are shown in Figure 6. Curves taken on some of these electrodes were used to determine the effects of NaHF_2 as a supporting electrolyte, and also of the effect of additions of water and NH_3 to the AHF. Typical curves are presented in Figures 5 and 6. As shown in Figure 5, there seems to be no appreciable modification of the curve produced by the NaHF_2 . Surprisingly, in Figure 6, no detectable alteration of the curves was produced by adding varying amounts of water up to a concentration which would produce a considerable current for an electroactive species in an aqueous electrolysis. Furthermore, addition of NH_3 to the AHF containing NaHF_2 did not produce a current wave comparable to that previously seen. The electrode used previously was not so highly fluorided as the one used for these experiments.

From these experiments, it is concluded that highly fluorided aluminum electrodes will not be useful at all for obtaining kinetic data on possible NH_3 electroreactions. In addition, the best remaining possible procedure for getting reproducible aluminum electrode behavior is to use a freshly prepared electrode each time a polarization curve is taken. This requires some modification of equipment which is described in another section.



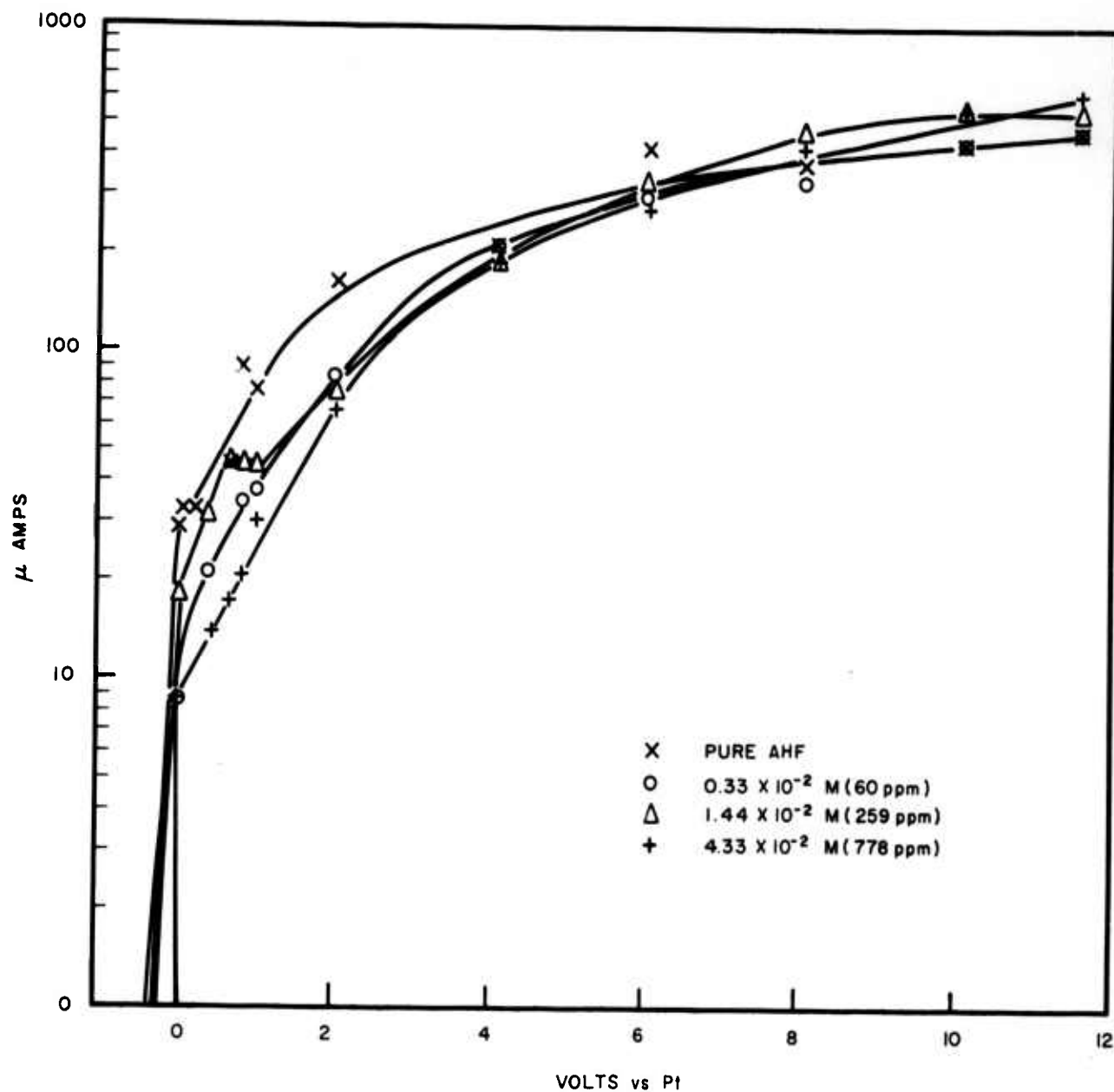
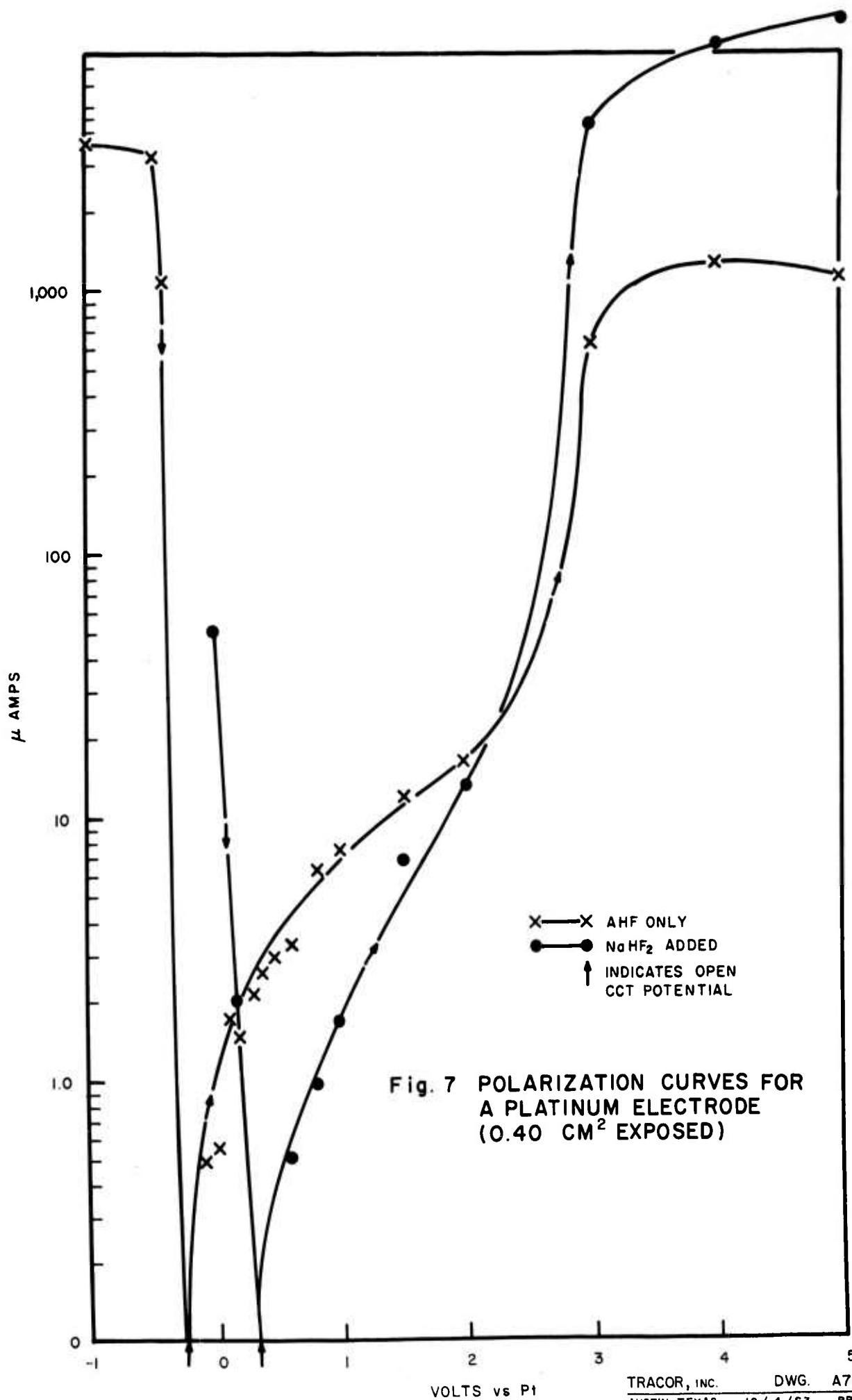


Fig. 6 - POLARIZATION CURVES IN AHF CONTAINING SMALL AMOUNTS OF WATER NaHF_2 PRESENT AS SUPPORTING ELECTROLYTE.



V. POLARIZATION CURVES ON PLATINUM

In previous reports (ref 3) the possibility was discussed of using a metal electrode which only slowly corrodes at the potentials required and thus contributes a relatively small and reproducible corrosion current which can be determined and subtracted out of the data. With this in mind a few experiments were carried out with platinum electrodes as the working anode. Typical results with and without NaHF_2 added are presented in Figure 7. These curves are indicative of a corrosion process involving F^- analogous to anodic curves seen on iron electrodes in basic aqueous media (ref 4). No further work is planned on platinum electrodes.

VI. DISCUSSION OF THE AVAILABLE DATA

The results of the experiments to date lead to some interesting conclusions regarding the electrofluoridation reactions of metals. First of all, nickel electrodes have usually been chosen because of the better current-voltage characteristics of cells using them (ref 5). From our current-time data taken at controlled potential and from the presence of NiF_2 at the bottom of the cell after electrolysis, the utility of nickel electrodes appears to be due to the fact that the NiF_2 spalls off periodically and thus produces a fresh, low impedance surface for the electrofluorination reaction. The current-time traces recorded at controlled potential coupled with the galvanostatic experiments show that the film thickness is not self-limiting as it is in the case of the formation of passive films on ferrous metals in aqueous solutions, but is instead analogous to film formation on the valve metals such as tantalum (ref 6). Further, the high impedance fluoride coatings are probably formed either by a field induced diffusion of F^- (or possibly HF_2^-) to the metal-fluoride interface or by a mixed diffusion of both Al^{+++} and F^- rather than by diffusion of Al^{+++} to the fluoride-electrolyte interface. This conclusion, based on our open circuit potential-time data, ties in with the conclusion of the Rocketdyne workers that gross surface effects are operative. The open circuit behavior after cathodic charging indicates the film has some porosity for H^+ and H_2 (or H).

These considerations bring to mind several directions to be taken in the search for a more useable electrode for electrode-kinetic studies. First, a decrease in the rate of film formation might be gained by using an acidic supporting electrolyte such as BF_3 or SbF_5 (ref 7) to suppress the dissociation formation of F^- . Second, a metal or alloy could possibly be found which either has a unit cell structure sufficiently different from that of its fluoride so that the film thickness becomes more nearly self-limiting, or which exhibits such a difference in the solubilities

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of the fluorides of two different ionic oxidation states (with the higher less soluble than the lower) that the film-growth behavior more nearly approximates that of passive ferrous metals in aqueous solutions. This solubility situation would be analogous to the hydrous oxides of iron(II) and iron(III).

VII. MODIFICATION OF THE ELECTROLYTIC CELL AND OF THE PROCEDURES

Since the last report, and as a result of the analysis of previous data, a porous Teflon divider has been provided to separate the anodic and cathodic compartments so that the product of the cathodic reaction (hydrogen) does not diffuse to the anode (or vice versa) and thus obscure the data. Two separate nitrogen lines have also been provided, one for each compartment so that sparging and stirring can be independently controlled in each. Also, a new Teflon cap for the cell is being fabricated so that the condensor can be offset and thus provide for insertion of the electrodes through the top instead of through the side as is presently done. Thus by using 1/8" diameter rods as electrodes and appropriate Swagelok fittings, the cell can be filled with AHF and then the electrodes inserted. They can also be withdrawn for visual and other examination immediately after use, so that changes in the nature of the surface coatings following different treatments can be observed and correlated. This modification should allow comparison of the behavior of the different electrodes under more nearly identical conditions and also provide for the use of a fresh platinum electrode each day to gain more reproducible base electrode potentials.

A heated NaF trap with a larger capacity than the previous one has been provided, and this has allowed a change in the AHF purification procedure, which has cut down the amount of time and effort necessary in this step. The tank AHF is now distilled into the trap operating at 110°C and then is distilled back into the vessel which was formerly used for electro drying. This vessel now serves only as a holding vessel for the dry AFH before transfer by distillation into the electrolytic cell. Using this procedure, 300 ml of AHF can be purified in one day and then held for weeks without the difficulties developing in the transfer lines which are caused by the muds and other corrosion products encountered previously.

VIII. FUTURE COURSE OF THE WORK

In a few experiments, the reproducibility of the polarization curves obtained from fresh aluminum electrodes in solutions containing F^- , HF_4 , and $HSbF_6$ will be checked. If any of the procedures improve the reproducibility, then experiments with solutions containing NH_3 will be started.

Reliability of the equipment has progressed to the point now that the conductivity and electrolytic experiments can be carried on simultaneously without a situation where one operation unduly influences the other. On this basis the conductivity measurements can be carried out so that each kind of experiment aids, rather than delays, the other. Concurrent conductivity and electrolytic experiments are planned for the immediate future.

The modification of the cell which will allow us to insert an electrode and take a polarization curve without the necessity of disassembling will permit taking data on different metals under the same conditions of exposure to the AHF (not possible previously). This will considerably simplify a survey of various metals to find one which is better suited for the need. Until a better electrode metal is found, it is planned to do these experiments either concurrently with the other work or very briefly so as to devote a minimum amount of time to work not specifically directed toward gaining kinetic and conductometric data. For this purpose, the following metals have been obtained in the form of 1/8" diameter rods suitable for electrodes: antimony, 99.999%; bismuth, 99.999%; cobalt, 99.6%; copper, 99.97%; iron, 99.9%; magnesium, 99.95%; silver, 99.9%; thallium, 99.999%; and titanium, 99.9%. These metals were selected both on the basis of previous experience (refs 8 and 9) and from a consideration of the solubilities of their fluorides (ref 10). It is hoped that one of those metals which have two oxidation states, with the fluoride of the higher oxidation state more insoluble than the lower, will possibly exhibit the type of passivity desired.

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